

Calorimetry and Thermogravimetry of Bound Water in Dried Milk and Whey Powders

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Abstract

Thermal data show that water is sorbed by milk and whey powders through primarily weak binding forces at low to intermediate relative humidities. Heat required to release and vaporize such bound water, as determined by differential scanning calorimetry is 10.1 ± 0.4 kcal per mole of water desorbed from whole or skim milk powders. When milk or whey powders sorb sufficient water, at $\geq 50\%$ relative humidity, to induce lactose crystallization or changes in protein conformation, the differential scanning calorimetry pattern becomes more complex, desorption is completed at a higher temperature and the enthalpy of desorption increases by 1.44 to 2.44 kcal per mole.

Introduction

The significance of water activity in the production and storage of almost all prepared foods is well-known. Hence, as part of research directed to develop new and improved dried dairy products, we have extensively studied their water binding properties.

Sorption isotherms for dried milk and whey powders and purified milk components in anhydrous form, demonstrating the magnitude of their water sorption capacities have been published (2,3). Expanded utilization of such data requires information concerning the energetics and the nature of the water vapor binding process. Thermodynamic treatment of multi-temperature sorption data (4) has yielded values for q_{st} the isosteric heat of adsorption of water by milk powders whereas this investigation is concerned with direct measurement of ΔH_w , the heat required to vaporize water bound to or associated with dried and humidified milk and whey powders. These heat quantities, q_{st} and ΔH_w , do not represent the same thermodynamic quantity with opposite signs, as q_{st} is a differential molar heat quantity defined by application of the Clausius-Clapeyron

equation with moles adsorbed held constant; and ΔH_w is experimentally determined with the specific conditions of differential scanning calorimetry. Values for ΔH_w , however, do reflect the binding energy in the sorption process and provide a direct indication of the energy requirements for water removal in dairy product dehydration.

Materials and Methods¹

Differential scanning calorimetry was employed to measure ΔH_w for water held by whey, skim milk, and whole milk powders conventionally spray-dried or foam-spray dried (8) in the Dairy Products Laboratory pilot plant. Determinations were made either with powders containing only the residual moisture after drying or with powders exposed to water vapor in humidostats controlled with appropriate saturated salt solutions (10).

Calorimetric standards used were: indium, lead and tin (Perkin-Elmer), benzoic acid (James Hinton, 99.99%, zone refined) naphthalene (James Hinton, 99.99%, zone refined), and anthracene (James Hinton, 99.99%, zone refined).

The Perkin-Elmer Model DSC-1B, differential scanning calorimeter was used to measure enthalpy. The temperature scale of the instrument was calibrated by the manufacturer's instructions using the melting points of high purity indium, lead, and tin. Calibration of the electrical output signal from the calorimeter for quantitative evaluation of the recorder tracings was performed by correlating the area under the endothermic peak for the melting of indium with its known heat of fusion ($\Delta H_f = 6.79$ cal/g). Peak areas were measured with a polar planimeter (Keuffel and Esser Company, K and E 4236). Measurements of ΔH_f for benzoic acid, naphthalene, and anthracene were made to check the scanning calorimeter and its calibration. These materials were scanned in sealed capsules (Perkin-Elmer

¹ Reference to certain products or companies does not imply an endorsement by the Department over others not mentioned.

volatile sample sealer accessory) to avoid errors due to sublimation. The ΔH_t values were within experimental error of those found by Hampson and Rothbart (7) and other values from the literature as tabulated by them.

In determining ΔH_w 5 to 20 mg of powder were packed in aluminum sample pans and scanned at a programmed heating rate of 10 C per minute over a suitable interval to obtain complete water desorption. We used either the standard crimped sample pans from the Perkin-Elmer Corporation which are not hermetically sealed and permit rapid removal of water vapor from the calorimeter cell in a stream of N_2 gas, or hermetically sealed capsules with a small pinhole punctured in the lid. The latter sample container restricts vapor removal requiring a higher temperature for complete desorption.

Precautions are necessary in dehydration studies to avoid transfer of water vapor between the sample and the atmosphere before scanning in the calorimeter. This was done by rapidly cooling the sample, in either container, to 0 C in the calorimeter cell before beginning the scan. Loss of moisture from the sample is negligible at 0 C and additional water uptake would not occur with flowing N_2 .

ΔH_w values were computed by measuring the area of the endothermic peak for dehydration and vaporization and correlating the quantity of absorbed heat with the mass of desorbed water. Water desorptions were measured by weighing the samples before and after the scanning run. These values agreed with parallel measurements of water content by evacuation at ambient or elevated temperature and by thermogravimetric analysis.

Thermogravimetric analyses were with a Cahn RG recording electrobalance and the "Little Gem" TGA accessory of the Cahn Instrument Company. Data were plotted as mass against temperature with a Varian Model 100 X-Y recorder. Samples were heated in a platinum bucket from ambient temperature (23 to 27 C) to 200 C at five degrees per minute.

The heating rate was controlled manually with a laboratory transformer as suggested in the Cahn instruction manual. The "Little Gem" accessory has no provisions for atmosphere control or desorbed vapor removal.

Results and Discussion

Heating foam spray-dried whole milk powder from 0 C to 200 C yielded the thermogram in Figure 1. There is a broad endothermic peak from water vapor desorption between 12 to 15 C and 130 to 132 C with a maximum at 67 to 72 C.

This peak is associated with water desorption being absent with powders previously dried under high vacuum. The association of this thermal event with a mass loss was also confirmed with the thermogravimetric analyses. The average heat value computed for several samples of foam spray-dried whole milk powder was $\Delta H_w = 557 \pm 19$ calories per gram of water desorbed. These data for whole milk and similar data for whey and skimmilk powders were from low-moisture powders never exposed to humidities greater than 50%.

The influence of previous water sorption on the shape of the scan is shown in Figure 2 for foam spray-dried skimmilk powder. These data are for samples previously held at relative humidities 20, 60, and 90% and allowed to sorb water until equilibrium conditions were reached. The curve for powder equilibrated at 20% relative humidity is similar to the whole milk scan of Figure 1 with $\Delta H_w = 562$ calories per gram of desorbed water.

The scans for powders exposed to higher relative humidities are strikingly different. Desorption endotherms in both cases are split into two peaks with the second peak extending from 90–95 C to approximately 145 C. Similar differences are present in the weight loss patterns from thermogravimetric analyses (Fig. 3). The powder originally held at low humidity lost its water in a single step completed at 125 C followed by decomposition and charring of the powder beginning around 135 C. Those exposed to 60 and 90% relative humidities both exhibited three mass loss stages, the third stage being decomposition and charring of the powder. The first two mass losses in the thermogravimetric analyses curves correspond to the two peaks observed with differential scanning calorimetry.

These data indicate physical-chemical differences in the binding of water by powders at different humidities and may be associated with changes in the constituent carbohydrates and proteins resulting from water sorption.

The powders equilibrated at 60 and 90% relative humidity were exposed to water vapor at relative pressures high enough to change amorphous lactose into the crystalline α -monohydrate (2). The second peak in the calorimetry scan and the second mass loss stage in the thermogravimetric analyses may be attributed to water of hydration bound in the crystal lattice of α -lactose. It has been demonstrated (6) by differential scanning calorimetry and thermogravimetric analyses of pure lactose that such water is more firmly bound and is released only at higher temperature and its desorption

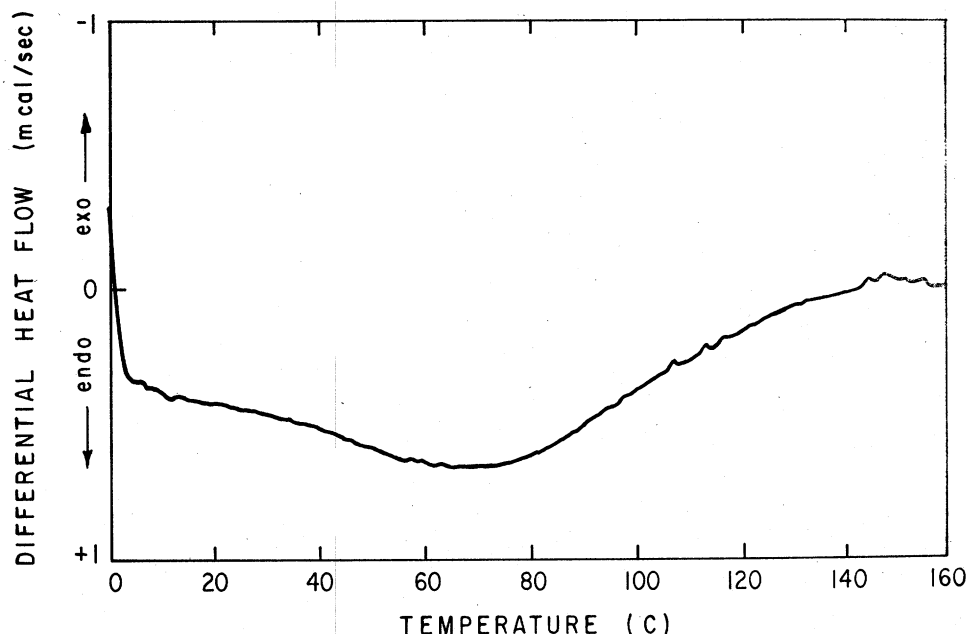


Fig. 1. Differential scanning calorimetric trace for 6.465 mg foam-spray-dried whole milk powder.

requires more energy, 680 calories per gram of water. When pure crystalline α -lactose monohydrate is heated in the differential scanning calorimeter, dehydration occurs in a single

discrete stage between 97 and 165°C whereas amorphous lactose is dehydrated continuously between 5 and 135°C. Hence, the peaks in the scans with milk and whey powders can be

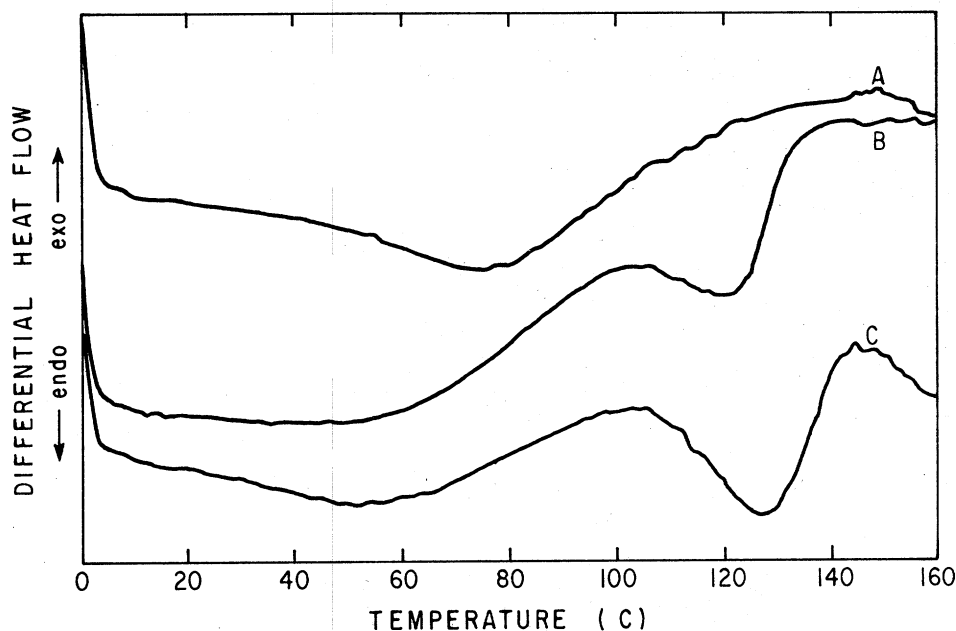


Fig. 2. Effect of water sorption on spray-dried skim milk powder. Differential scanning calorimetric traces for: A—4.990 mg, held at 20% RH^a; B—4.710 mg, held at 60% RH; C—4.620 mg, held at 90% RH.

^a Relative humidity.

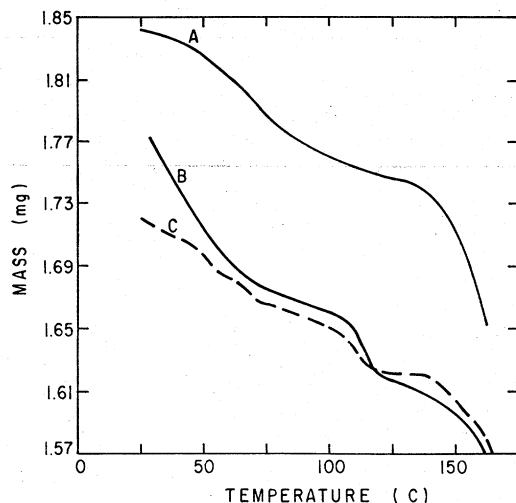


FIG. 3. Thermogravimetric curves for skim milk powder held at: A—20% RH; B—60% RH, and C—90% RH.

understood as the effects of lactose crystallization. Furthermore, excellent agreement was observed on comparison of the mass lost in the second thermogravimetric analyses step with the mass of water calculated to be present as water of hydration from results of a Sharp and Doob (11) determination of the α -lactose in the powder.

The first scanning peak represents water

held less rigidly which is desorbed at a lower temperature. This is water bound either by protein or by lactose in the amorphous state. These results agree with our previous investigations of lactose (6) and protein dehydration (5). Values of ΔH_w are given in this paper for low to intermediate relative pressures only as it is impossible to compute energy values when lactose has crystallized and the desorption peak has split because of uncertainties in assigning a position to the baseline. Rescanning the powders after desorption to establish the baseline is unsuitable even using specialized methods which account for changes in specific heat because it is impossible to independently account for specific heat changes due to each dehydration stage since they are not completely separated in these traces.

The effects of water sorption on the scanning pattern of whey powder is evident from the traces in Figure 4 obtained with whey powders previously held at 45 and 95% relative humidity. The curve for the powder held at the lower humidity is almost identical to dehydration curves for lactose glass (6). This is logical because powdered whey normally contains approximately 70% lactose which is almost entirely in the glass form unless special methods are used to intentionally induce crystallization. The curve for the whey powder held at 95% relative humidity has two distinct peaks which

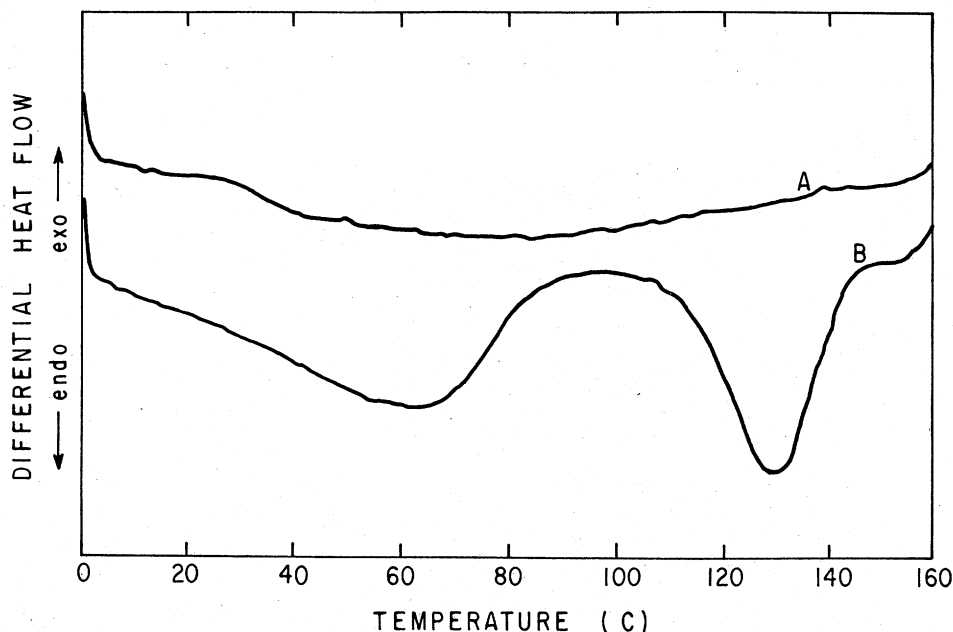


Fig. 4. Differential scanning calorimetric traces for whey powders, kept in humidostats: A—7.480 mg, held at 45% RH for 25 hr; B—7.865 mg, held at 95% RH for 23 hr.

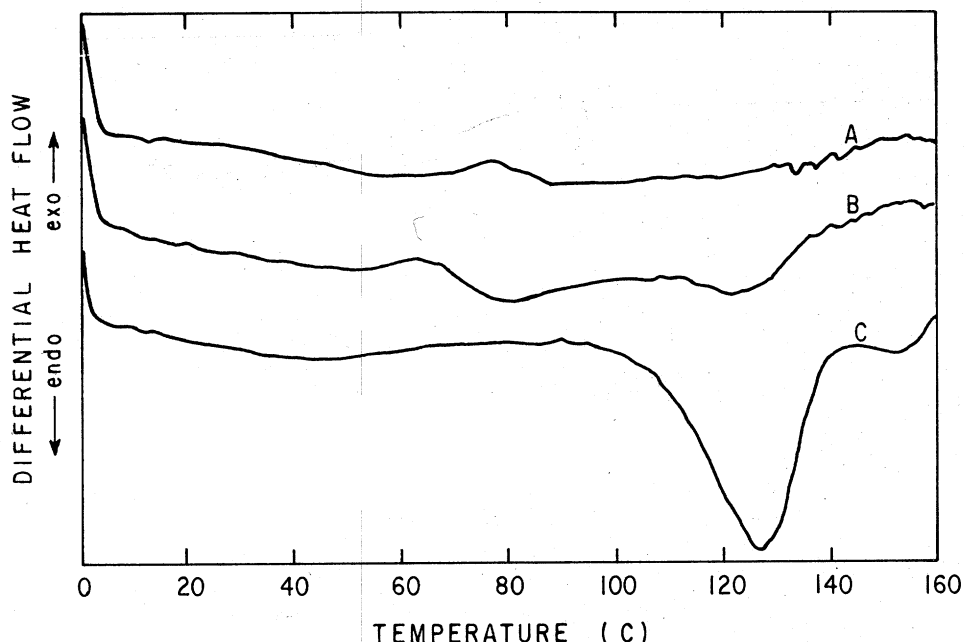


FIG. 5. Desorption patterns for whey powders held at 75% RH: A—6.360 mg, after 24 hr; B—7.055 mg, after 29 hr; and C—6.690 mg after 46.5 hr.

may be explained in a manner identical to that employed with the skimmilk powders.

The concept of a physical change in powder during water sorption is supported by the data in Figure 5 for whey powder held at 75% relative humidity for different periods. Comparison of these curves clearly indicates mobility of sorbed water until equilibrium conditions are attained when a large fraction of sorbed water becomes water of hydration of α -lactose monohydrate.

The values for ΔH_w in this paper are similar to the heat of vaporization of pure liquid water which we found to be 550 ± 23 calories per gram in 15 separate determinations. This similarity indicates only weak binding in the relative pressure range for which ΔH_w values were calculated. Differential scanning calorimetry of pure samples of lactose and milk proteins which sorbed water at higher relative humidities yielded higher values for ΔH_w . These enthalpies were 80 to 125 calories per gram higher than the heat of vaporization of liquid water (5,6).

Thus, it may be concluded that stronger binding of water with milk and whey powders occurs only after sufficient water is sorbed to crystallize lactose or change configuration of the protein (5).

It is of interest that the characteristic thermal profile of butteroil (1,13) was not observed in any of the scans with whole milk

powder even after previous drying. The absence of these peaks may be because of the low concentration of materials or the effects of a combination of protein, lipid, and water on the thermal behavior of the lipid in preventing or retarding the occurrence of certain thermal transitions (9,12). More fundamental information concerning the physical chemical structures involving proteins, lipids and water is needed to answer such questions for milk powder and other heterogeneous systems.

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